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Effects of NO_X Storage Component on Ammonia Formation in TWC for Passive SCR NO_X control in Lean Gasoline Engines

Author, co-author (Do NOT enter this information. It will be pulled from participant tab in MyTechZone)

Affiliation (Do NOT enter this information. It will be pulled from participant tab in MyTechZone)

Abstract

A prototype three-way catalyst (TWC) with NO_X storage component was evaluated for ammonia (NH_3) generation on a 2.0-liter BMW lean burn gasoline direct injection engine as a component in a passive ammonia selective catalytic reduction (SCR) system. The passive NH_3 SCR system is a potential approach for controlling nitrogen oxides (NO_X) emissions from lean burn gasoline engines. In this system, NH_3 is generated over a close-coupled TWC during periodic slightly-rich engine operation and subsequently stored on an underfloor SCR catalyst. Upon switching to lean, NO_X passes through the TWC and is reduced by the stored NH_3 on the SCR catalyst. Adding a NO_X storage component to a TWC provides two benefits in the context of a passive SCR system: (1) enabling longer lean operation by storing NO_X upstream and preserving NH_3 inventory on the downstream SCR catalyst; and (2) increasing the quantity and rate of NH_3 production during rich operation. Since the fuel penalty associated with passive SCR NO_X control depends on the fraction of time that the engine is running rich rather than lean, both benefits (longer lean times and shorter rich times achieved via improved NH_3 production) will decrease the passive SCR fuel penalty. However, these benefits are primarily realized at low to moderate temperatures (300-500 °C), where the NO_X storage component is able to store NO_X, with little to no benefit at higher temperatures (>500 °C), where NO_X storage is no longer effective. This study discusses engine parameters and control strategies affecting the NH_3 generation over a TWC with NO_X storage component.

Introduction

Concerns about greenhouse gas emissions and dependence on petroleum have motivated governments around the world to develop regulations that require significant improvements in vehicle fuel economy. In the U.S., the projected fuel economy compliance levels for light duty vehicles will require the average fuel economy to increase to 54.5 miles per gallon by 2025, which is more than 50 % higher than the current regulations. These regulations have motivated vehicle manufacturers to pursue a range of technologies that reduce petroleum consumption. To ensure their adoption in the marketplace, these technologies must comply with increasingly stringent exhaust emissions regulations for pollutants such as nitrogen oxides (NO_X), carbon monoxide (CO), hydrocarbons (HCs), and particulate matter (PM). The U. S. Environmental Protection Agency Tier 3 emissions regulations require more than 80 % reduction in NO_X and non-methane HCs from the previous Tier 2 Bin 5 emission standard. Meeting both the 2025 CAFE standards for fuel economy and the Tier 3 emissions regulations will require significant advancements in engines, powertrains, and emissions control.

In the U.S., the light duty vehicle fleet is dominated by gasoline engines operating at stoichiometric air-to-fuel ratios (AFR) [1]. Stoichiometric exhaust conditions are ideal for a three-way catalyst (TWC) to effectively control NO_X, CO, and HC emissions to regulated levels. Lean operation can increase the fuel economy of a gasoline engine by 10-20 % over stoichiometric operation [2], [3]. While TWCs can effectively oxidize CO and HCs under lean conditions, they are unable to reduce NO_X in the presence of excess oxygen; thus, a different emissions control technology is required for the abatement of NO_X emissions from lean burn gasoline engines. While urea-based selective catalytic reduction (SCR) has proven effective in controlling NO_X emission from diesel vehicles, the urea storage and delivery components can add significant cost and weight to the vehicle. As such, onboard NH_3 production via a passive SCR approach is of interest [4], [5]. In a passive SCR system, NH_3 is generated over a close-coupled TWC during periodic slightly rich operation and subsequently stored on an underfloor SCR catalyst. Upon switching to lean, NO_X passes through the TWC and is reduced by the stored NH_3 on the SCR catalyst. This approach is particularly attractive for lean gasoline engines because it makes use of a TWC that is already onboard and eliminates or greatly reduces the need for a urea system.

The effectiveness of a passive SCR system depends on efficient and selective NH_3 generation and utilization over the TWC+SCR catalysts. Since the rich operation necessary for NH_3 generation incurs a fuel consumption penalty, minimizing the duration and magnitude of rich excursions is critical and requires a combination of

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engine management and emissions control optimization. During rich/lean cycling, NH_3 produced while rich and NO_X concentration when lean ultimately control cycle timing and fuel consumption [6], [7]. The fuel efficiency of the passive SCR approach, therefore, benefits from high engine out NO_X during rich operation for NH_3 production, and low engine out NO_X during lean operation which consumes less NH_3 on the SCR catalyst. A number of engine controls including air-fuel equivalence ratio, spark timing, valve timing and exhaust gas recirculation can be utilized to maximize engine out NO_X during rich operation and minimize engine out NO_X during lean operation [6]. Another potential approach to increase lean operation time is to utilize a TWC with a NO_X storage component. Adding a NO_X storage material to a TWC can potentially enable longer lean operation by storing some of the NO_X. The objective of this work is to investigate the implications of adding a NO_X storage component to a TWC in a passive SCR approach.

Experimental Setup

Engine Platform

All experiments were conducted on a lean gasoline engine coupled to a motoring direct current dynamometer that controls the engine speed and load. The engine was removed from a European Model Year (MY) 2008 BMW 1-series 120i (E87) vehicle. It is a 4-cylinder 2.0-liter naturally aspirated direct injection gasoline engine that has a rated power of 125 kW at 6700 revolutions per minute (rpm) and a torque of 210 Nm at 4250 rpm. Table 1 summarizes engine specifications.

Table 1. BMW 2.0-liter lean direct injection engine specifications.

Engine Model Number	N43B20
Displaced volume	1995 cm^3
Number of cylinders	4
Stroke	90 mm
Bore	84 mm
Compression ratio	12.0:1
Rated Power	125 kW at 6700 rpm
Rated Torque	210 Nm at 4250 rpm

The engine was operated on an EEE-Lube Certification Gasoline (Haltermann Solutions) with low sulfur levels. Table 2 shows key gasoline fuel properties provided by the vendor.

Table 2. EEE-Lube Cert Gasoline fuel properties.

Lower Heating Value, kJ/kg	42715
Density, kg/liter	0.742
C, weight fraction	0.8598
H, weight fraction	0.1314
Oxygen, weight %	<0.01
Sulfur, mg/kg	4
Aromatics, volume %	27.4
Olefins, volume %	0.9
Saturates, volume %	71.8
Research Octane Number (RON)	96.4
Motor Octane Number (MON)	88.4

The engine uses a spray guided combustion system design. In this design, a piezoelectric injector is located at the top center of the combustion chamber, with a spark plug in close proximity to the injector. This geometry allows ignition of the fuel as it is injected, which results in shorter mixture formation time compared to wall guided and air guided combustion systems [8]. With shorter mixture formation time, lean engine operation can be extended to higher speeds and loads, resulting in additional fuel savings. The overall air-fuel equivalence ratio, or λ (ratio of actual AFR to stoichiometric AFR), during lean operation ranges between 1.3 and 2.2. Up to 20 % reduction in fuel consumption can be achieved with lean operation relative to stoichiometric. The engine, however, only operates lean over a portion of the engine's speed and load range (up to 4500 rpm and 75 % load). Outside the lean operating range, at higher engine speeds (>4500 rpm) and loads (>75 %), the engine operates in the stoichiometric combustion mode. The engine can also operate in the stoichiometric mode over its entire operating range. For this study modifications to the stoichiometric mode were made in order to operate the engine rich ($\lambda<1$) for NH_3 generation. Details on an additional rich combustion strategy available on this engine can be found in a previous publication [9].

The factory engine control unit was replaced with a custom full-pass control system developed by National Instruments - Powertrain Controls Group. The controller mimics the original equipment manufacturer (OEM) combustion strategies and, furthermore, enables full control of all engine parameters, including fuel injection quantity and timing, spark timing, λ, and EGR rate, which allows full control of the different modes of combustion. Additional information on the engine setup, performance and emissions can be found in [2], [3], [9].

TWC with NO_X Storage Component (NSC)

A prototype TWC with NSC used in the present investigation was provided by Umicore. The catalyst formulation contains platinum (Pt), palladium (Pd), rhodium (Rh), and oxygen and NO_X storage materials. The catalyst details are summarized in Table 3. A 1.3-liter catalyst monolith was installed in the engine exhaust in a close-coupled configuration. Prior to evaluation, it was degreened in the engine exhaust for approximately 20 hours with a maximum inlet temperature of 850 °C.

Table 3. Umicore TWC with NSC details

Pt/Pd/Rh loading (g/liter)	Oxygen storage component	NO_X storage component
2.47/4.17/0.05	Yes	Yes

Emission Sampling

Raw exhaust was sampled at the pre- and post-TWC locations. The sample was routed through a heated filter prior to analysis. A California Analytical Instruments (CAI) heated flame ionization detector (FID) and paramagnetic detector were used to measure total unburned hydrocarbons and oxygen, respectively. An MKS

Instruments MultiGas Model 2030 HS FTIR Spectrometer with a heated 5.11 m multipass gas cell was utilized to measure multiple gases, including CO, CO_2, nitrogen monoxide (NO), nitrogen dioxide (NO_2), nitrous oxide (N_2O) and ammonia (NH_3). A magnetic sector mass spectrometer with a capillary sampling system (SpaciMS) was used to measure H_2. Details on the SpaciMS technique can be found in the publication by Partridge et al. [10]

Experimental Conditions

Steady-state λ sweeps

Steady-state λ sweeps were carried out to evaluate NO_X to NH_3 selectivity and reductant (HC, CO and H_2) utilization in the TWC under steady-state rich engine operation ($\lambda<1$). The λ sweeps were performed over a number of engine speed and load conditions providing a wide range of exhaust temperatures and space velocities as shown in Table 4. For these experiments, the OEM stoichiometric combustion mode was utilized, and fueling quantity was adjusted to achieve the desired rich λ.

Table 4. Steady-state operating points used in λ sweep experiments with corresponding catalyst inlet temperatures and space velocities

Speed (rpm)	BMEP (bar)	TWC inlet T (°C)	TWC SV (h^{-1})
2000	3	436	39K
2000	5	514	50K
2000	8	625	71K

Lean/rich cycling experiments

To assess TWC performance and fuel penalty from NH_3 generation under realistic operating conditions, a series of rich/lean cycling experiments were performed, where the engine alternated between rich and lean operation. These experiments were designed to be representative of the conditions a passive SCR system would encounter under realistic driving conditions. Load step and fixed load cycling experiments were carried out to simulate "hill" (acceleration) and "cruise" driving conditions, respectively. In load step experiments, the engine alternated between rich operation at 8 bar brake mean effective pressure (BMEP, a measure of engine load) and lean operation at 3 or 5 bar BMEP while maintaining 2000 rpm engine speed. The load was fixed at 3 or 5 bar BMEP for both lean and rich portions of the cycle during the fixed load experiments. The lean/rich cycling experiments details are summarized in Table 5 and Table 6 for the fixed load and load step cycling, respectively.

A feedback control strategy based on cumulative NH_3 produced by the TWC during rich operation and NO_X emissions during lean operation was implemented with the engine controller. In this manner, control setpoints for cumulative NH_3 production and NH_3:NO_X ratio allowed control of the lean/rich cycle timing to achieve the desired NH_3:NO_X ratio. The NH_3:NO_X ratio of 1 was used for all cycling experiments, and represents the theoretical stoichiometry for the standard SCR reaction between NH_3 and NO_X ($4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6\,H_2O$) on a SCR catalyst. The rich cycle timing was such that the NH_3 produced during rich operation would use approximately 25 % of the NH_3 storage capacity of the SCR catalyst (0.027 mol per liter of catalyst) based on prior flow reactor measurements. The NH_3 capacity utilization was intentionally kept low to prevent NH_3 slip during the lean phase, which was observed in flow reactor experiments with higher NH_3 loadings.

Table 5. Average experimental conditions for fixed load rich/lean cycling experiments conditions

	3 bar Fixed Load		5 bar Fixed Load	
	Lean	Rich	Lean	Rich
Speed, rpm	2000	2000	2000	2000
BMEP, bar	3	3	5	5
λ	1.76	0.90-0.99	1.47	0.90-0.99
inlet T, °C	393	412	494	510
SV, h^{-1}	45K	29K	56K	42K

Table 6. Average experimental conditions for load step rich/lean cycling experiments conditions

	3 bar Load Step		5 bar Load Step	
	Lean	Rich	Lean	Rich
Speed, rpm	2000	2000	2000	2000
BMEP, bar	3	8	5	8
λ	1.74	0.90-0.99	1.48	0.90-0.99
inlet T, °C	411	516	521	575
SV, h^{-1}	45K	61K	57K	60K

Results and Discussion

Steady-state λ sweeps

Steady-state λ sweeps were carried out to quantity how exhaust composition changes with variations in the air-fuel equivalence ratio under steady state engine operating conditions. Figure 1 shows emission concentrations in the exhaust as a function of λ at TWC inlet (a) and outlet (b) locations with the engine operating at a 2000 rpm 5 bar BMEP point. For $\lambda<1$, the mixture of fuel and air in the combustion chamber contains excess fuel, and there is insufficient oxygen to burn all the fuel, which results in increase of unburned hydrocarbons (HC) and partial oxidation products (CO and H_2). As shown in Figure 1a, as the amount of excess fuel increases, these emissions increase steadily with decreasing λ, with a much sharper increase in CO and H_2 concentrations. In a SI engine, the HC emissions are primarily formed in the crevices of the combustion chamber and the oil film layer [11], [12], where the flame cannot propagate making them less sensitive to changes in λ. On the contrary, the CO and H_2 emissions form at the flame front zone by incomplete oxidation of HC compounds, that are controlled by λ, and rise rapidly as the mixture becomes richer. NO_X forms in the hot burned zone, after the flame front, and its formation strongly depends on temperature and oxygen concentration. As the mixture is enriched, the temperature and the oxygen concentration fall, and NO_X emissions decrease.

The exhaust composition changes substantially as it passes through the TWC as shown in Figure 1b. At stoichiometric conditions, the TWC is very effective in converting the three regulated pollutants (CO, HC and NO_X) to CO_2, H_2O and N_2. At these conditions, there are enough reductants to reduce NO_X and enough oxygen to oxidize CO and HC. The range of λ near stoichiometric, where high conversion efficiencies of these three pollutants are achieved, is very narrow, and with a slight deviation from the stoichiometric exhaust conditions, the catalyst can no longer effectivity do CO and HC oxidation, and NO_X reduction. In the fuel-lean exhaust, the TWC is very active in removing CO and HC emissions, but the excess oxygen prevents NO_X reduction. In the fuel-rich exhaust, all the oxygen that is present in the exhaust gets consumed by an equivalent amount of CO, H_2 and HC. As the mixture gets richer, there is insufficient oxygen present in the exhaust for complete oxidation of CO and HC, and their concentrations increase. In a TWC, CO and HC can also be consumed through water gas shift (WGS) and steam reforming reactions, as shown in Equations 1 and 2, respectively.

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (1)$$

$$C_nH_m + nH_2O \rightarrow \left(\boldsymbol{n} + \frac{\boldsymbol{m}}{\boldsymbol{2}}\right) H_2 + nCO \qquad (2)$$

Under rich conditions, the NO_X reduction activity is very high. The TWC converts the incoming NO_X to a mixture of N_2 and NH_3 as shown in Figure 1b, with selectivity to NH_3 strongly depending on λ. To further illustrate this point, the concentration of NO_X and NH_3 at the TWC inlet and outlet locations, respectively, are plotted in Figure 2. As the mixture gets richer, the concentration of NH_3 sharply increases as λ decreases until it reaches a maximum at $\lambda = 0.96$, and then slowly decreases with lower λ values as the feed gas NO_X level decreases. The inlet NO_X and outlet NH_3 concentrations are identical for $\lambda < 0.96$, indicating that all of the NO_X is converted to NH_3. In this λ region, NH_3 formation is limited by the NO_X availability at the catalyst inlet. For $\lambda > 0.96$, on the other hand, the NH_3 generation is limited by the reductant availability, as illustrated by the decreasing concentration of HC, CO and H_2 in Figure 1a, and as λ increases the reduction of NO_X becomes more selective to N_2.

The results shown thus far indicate that λ is a critical parameter in controlling engine and TWC exhaust composition. In the context of generating desired levels of NH_3, the two important but competing processes occur as the mixture is enriched: richer mixtures generate reductants that in turn control NH_3 selectivity, but richer mixtures also decrease engine-out NO_X, thus, limiting NO_X available for the TWC to generate NH_3. In addition, the rich operation necessary for NO_X to NH_3 reduction results in a fuel consumption penalty, which is another constraint, and must be considered when selecting the appropriate operating λ to meet NH_3 demands while minimizing fuel consumption penalty. Of course, HC and CO emission must also be considered.

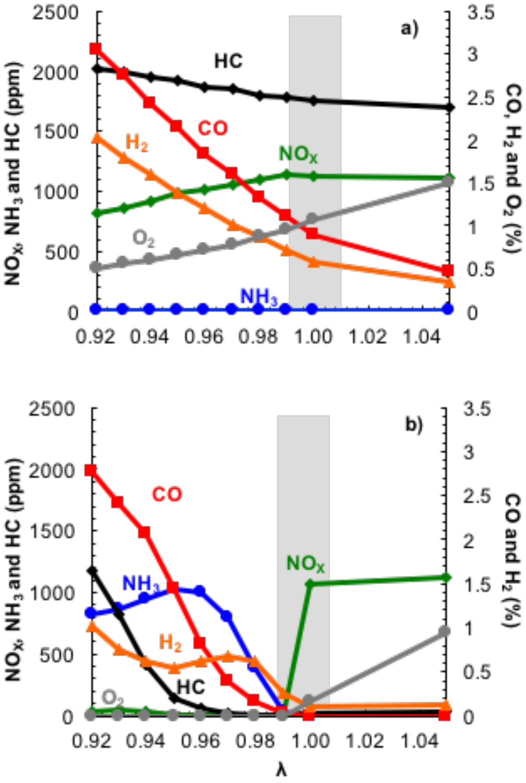

Figure 1. Steady-state gas concentration at (a) TWC inlet and (b) TWC outlet as a function of λ. Engine operating conditions: 2000 rpm and 5 bar BMEP. TWC at 514 °C inlet temperature and 50K h^{-1} space velocity.

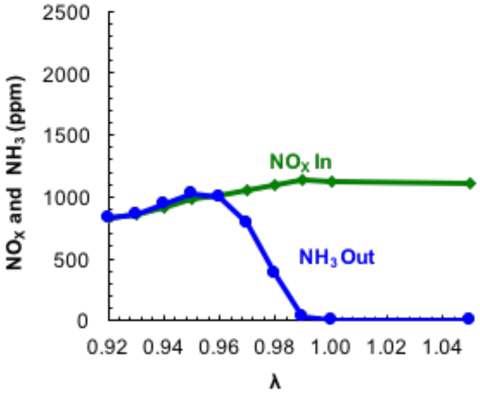

Figure 2. Steady-state concentration of inlet NO_X and outlet NH_3 as a function of λ. Engine operating conditions: 2000 rpm and 5 bar BMEP. TWC at 514 °C inlet temperature and 50K h^{-1} space velocity.

The results presented in Figures 1 and 2 were collected while the engine was operating at 2000 rpm and 5 bar BMEP. Similar trends were also observed at other steady-state engine operating points listed in Table 4. To summarize the influence of λ on the NH_3 production during steady-state rich operation, NH_3 yield at different λ values is plotted in Figure 3 for each of the operating points evaluated. The NH_3 yield is defined as

$$\mathbf{NH_3}_{\,\boldsymbol{yield}} = \frac{\mathbf{NH}_{\mathbf{3}\,\boldsymbol{out}}}{\mathbf{NO}_{\boldsymbol{X}\,\boldsymbol{in}} + \mathbf{NH}_{\mathbf{3}\,\boldsymbol{in}} + \mathbf{2\,N_2O}_{\boldsymbol{in}}} * \mathbf{100\%} \qquad (3)$$

NH_3 yield increases as the exhaust mixture gets richer for all the engine operating points, reaching greater than 90% yield at $\lambda = 0.96$. The results show that this TWC is able to produce high NH_3 yields at slightly rich conditions over a wide range of temperatures and space velocities. High NO_X to NH_3 conversion was achieved in the 430-625 °C temperature range and 40-70K h^{-1} gas hourly space velocity range with $\lambda \leq 0.96$. A decreasing trend in the NH_3 yield is observed at higher engine loads and is due to increasing exhaust temperatures; this observation is consistent with results from bench flow reactor studies by Pihl et al. showing decrease in NH_3 yield at temperatures greater than 500 °C for the same catalyst [13].

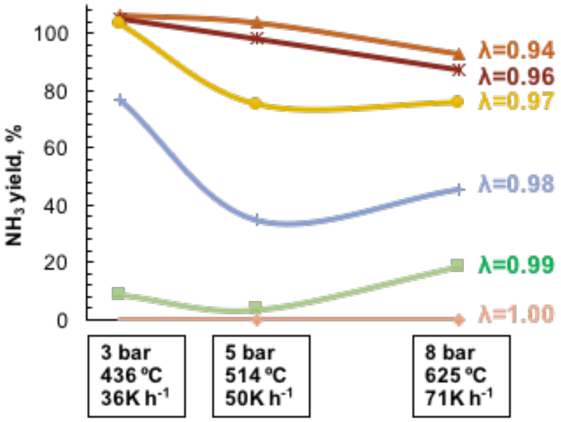

Figure 3. Steady-state NH_3 yield at different λ values at 2000 rpm engine speed and 3, 5 and 8 bar BMEP engine loads. See Table 4 for corresponding catalyst temperatures and space velocities.

The results from steady-state λ sweeps show that NH_3 can be generated in a wide range of engine operating conditions, and is limited by the air-fuel equivalence ratio and the amount of inlet NO_X. Thus, λ and engine-out NO_X emissions are primary parameters affecting NH_3 generation, which in turn controls rich timing and fuel consumption of the passive SCR system. The passive SCR approach would, therefore, benefit from high engine out NO_X during rich operation and high NH_3 selectivity at λ values as close to stoichiometric as possible.

Lean/rich cycling experiments

In the experiments above, the steady-state results were obtained under continuous rich engine operation with the catalyst being in a reduced state. In a passive SCR application, the TWC is exposed to both lean and rich exhaust, where the catalyst undergoes oxidation and reduction processes. The redox state can change NH_3 formation characteristics [14], [15], particularly for a TWC that contains oxygen and NO_X storage materials. As shown in Figure 4, the TWC with NO_X storage component studied here can yield much higher levels of NH_3 during the rich phase of lean/rich cycling compared to steady-state rich operation at the same engine operating point. In this section, the performance of this TWC under lean/rich cycling operation is discussed.

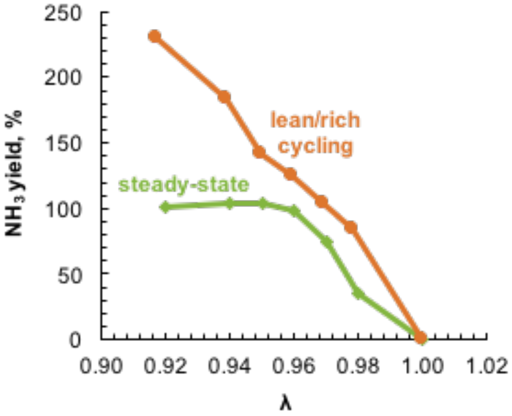

Figure 4. NH_3 yield during steady-state and lean/rich cycling experiments as a function of λ at 2000 rpm 3 bar BMEP engine operation.

The NH_3 formation and reductant utilization over the TWC were studied under lean/rich cycling operation representative of the conditions a passive SCR system would encounter under realistic driving. The TWC studied here contains a NO_X storage component, which demonstrated NO_X removal during lean operation as expected and, subsequently, led to an unexpected sharp rise in NH_3 production in the initial phase of rich engine operation.

The emissions of NO_X, NH_3, N_2O, CO and HC at the TWC inlet and outlet during the fixed load experiments with rich $\lambda = 0.96$ are shown in Figure 5. The average inlet catalyst temperature in the lean phase is 393 °C. At this temperature, the NO_X storage properties of the TWC are observed as evidenced by the delay in the NO_X breakthrough. The NO_X begins to break through early in the lean phase and steadily increases until it reaches the feed gas NO_X levels, approximately 2 minutes into the lean phase. As the cumulative NO_X reaches the threshold, the engine switches to rich operation. As soon as this happens, the effluent NO_X concentration drops to zero and stays at this level through the duration of the rich phase. After a short delay, a sharp transient increase in NH_3 production during the early onset of rich engine operation is observed, which quickly decreases to steady-state levels of the feed gas NO_X, indicating that all of the feed gas NO_X is converted to NH_3. This sharp NH_3 production was not observed on a Pd-only TWC studied previously as shown in Figure 6b [6], and contributed to the NO_X storage component of the TWC, in which some of the stored NO_X is converted to NH_3 upon switching to rich conditions. However, such large NH_3 production was unexpected as the results from the previous bench flow reactor study of the same catalyst under similar simulated exhaust conditions did not show a sizeable NH_3 peak on transition from lean to rich, and most of the stored NO_X was reduced to N_2 [13] as shown in Figure 6c. The sharp increase in NH_3 production is attributed not only to the NO_X storage characteristic of the TWC, but also to the transient response of the engine when it switches from lean to rich. The transition time from lean to rich (and vice versa) is about 1 second. During this 1 second transient, the engine controller temporarily overshoots the target $\lambda = 0.96$ to much richer $\lambda \sim 0.8$ and produces a large flux of reductants, as indicated by the spikes in engine out CO and HC emissions. The increased availability of reductants drives the reduction of the stored NO_X to NH_3. Such rapid NH_3 production can be beneficial during transient driving conditions with limited time at high load operation. This transient, often referred to as a "tip-in", is a primary contributor to the size of the peak of NH_3 production during rich operation.

Similar to steady-state experiments, N_2O emissions are not observed during the rich phase of lean/rich cycling experiments; however, small traces of N_2O (~2ppm) are detected during the lean portion of the cycle. The 40 ppm N_2O spike is observed right on the switch from lean to rich, which is followed by the onset of NH_3 production. This underlines the complex competitive reduction of NO_X on the catalyst surface when the TWC transitions through oxidation/reduction processes [16], [17]. The peak and width of the N_2O spike decreases at higher temperatures (as in the case of 2000 rpm 5 bar BMEP cycling) and richer λs, respectively. N_2O formation is important due to its high global warming potential (298 times that of CO_2) [18] . Even low levels of N_2O can have a high impact on greenhouse gas emissions, and if not carefully controlled, N_2O will reduce the overall benefit of the passive SCR approach.

The delay in NH_3 production, during which the N_2O is also formed, coincides with high initial CO and HC conversion. Subsequently, when oxygen is depleted from the catalyst surface and the reducing conditions are established, the CO and HC emissions begin to slip through the duration of the rich phase. At richer λ, this delay is minimized, and the onset of NH_3 production and CO and HC slip begin immediately on the transition from lean to rich. This further emphasizes the importance of the tip-in in the case of a TWC with OSC where extra reductants are needed to remove the stored oxygen and reduce the delay in NH_3 production. However, an excessively rich λ should be avoided in order to minimize the CO and HC slip and fuel consumption.

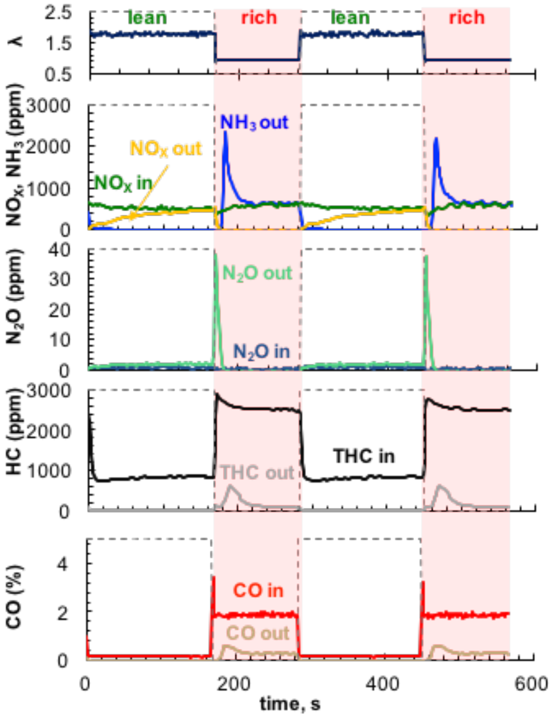

Figure 5. λ and emissions at TWC inlet and outlet as a function of time during fixed load lean/rich cycling experiments. Lean conditions: 2000 rpm 3 bar BMEP, λ=1.76, ave. T_{IN}=393 °C, SV=45K h^{-1}. Rich conditions: 2000 rpm 3 bar BMEP, λ=0.96, ave. T_{IN}=412 °C, SV=29K h^{-1}.

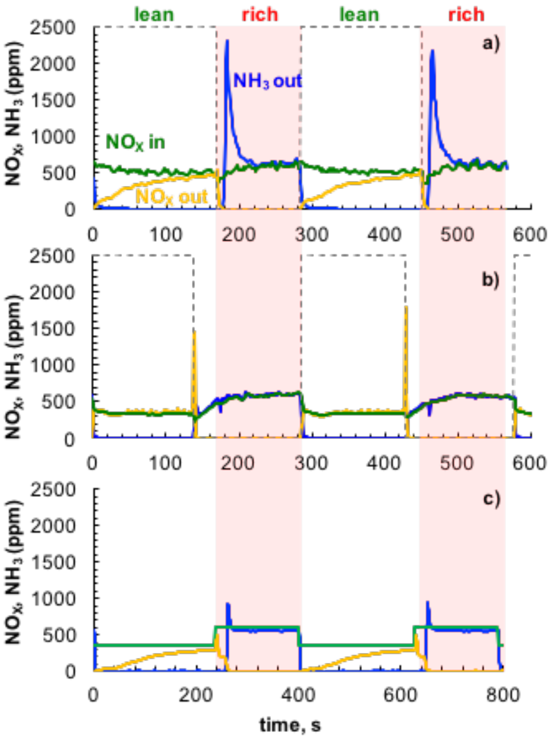

Figure 6. NO_X and NH_3 emissions at TWC inlet and outlet as a function of time during fixed load lean/rich cycling experiments on (a) engine with TWC containing NSC, (b) engine with Pd-only TWC and (c) bench flow reactor with TWC containing NSC under similar conditions.

To summarize the influence of rich λ on the NH_3 production during the fixed load lean/rich cycling experiments, engine out NO_X concentrations entering the TWC and corresponding exiting NH_3 concentrations during the rich phase are plotted in Figure 7. As shown in Figure 7a, the NH_3 concentration exiting the TWC significantly exceeds the inlet NO_X concentration under rich conditions. At 2000 rpm 3 bar BMEP fixed load cycling, the average inlet catalyst temperature in lean phase is 393 °C. At this temperature, some of the NO_X is stored and upon switching to rich, some of the stored NO_X is converted to NH_3. The conversion of the stored NO_X to NH_3 increases with richer λ as shown in Figure 8, reaching 100 % stored NO_X to NH_3 conversion at λ = 0.92. The NO_X storage component, therefore, offers two benefits in the context of a passive SCR system. First, by storing NO_X during the lean phase, it enables longer lean operation for a fixed inventory of NH_3, and second, by converting some of the stored NO_X to NH_3, shorter rich times are needed to produce a fixed dose of NH_3. Since the fuel penalty associated with passive SCR NO_X control depends on the fraction of time that the engine is running rich rather than lean, both longer lean times and shorter rich times will decrease the passive SCR fuel penalty.

However, these benefits can only be realized when NO_X is stored on the catalyst. The amount of NO_X this TWC can store decreases at higher temperatures, so the benefit can primarily be realized at low to moderate temperatures (300-500 °C) with little to no benefit at higher temperatures [13]. At higher operating temperatures, where the catalyst shows limited NO_X storage activity, there is no NH_3 production spike at the rich onset, and NH_3 generation is limited to feed gas NO_X concentrations as shown in Figure 7b. The average inlet catalyst temperature in lean phase is 494 °C for this case, and there is limited NO_X storage at this temperature. These results show that a TWC with NO_X storage component can enable increased NH_3 production with benefits strongly depending on the temperature and rich λ. The temperature dictates how much NO_X is stored and rich λ dictates how much and how rapidly stored NO_X is converted to NH_3.

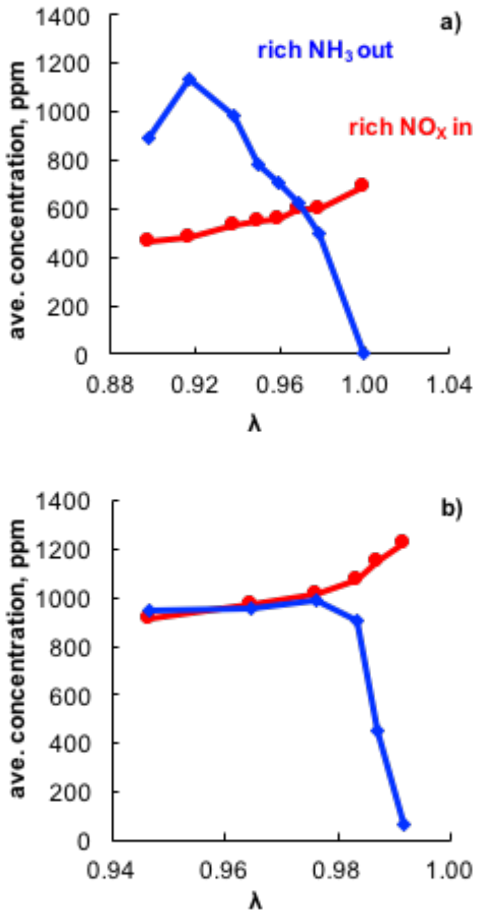

Figure 7. Engine out NO_X concentration entering ("rich NO_X in") the TWC and corresponding exiting NH_3 concentration ("rich NH_3 out") during rich phase of fixed load lean/rich cycling experiments at a) 2000 rpm 3 bar BMEP, lean ave. T_{IN}=393 °C, rich ave. T_{IN}=412 °C and b) 2000 rpm 5 bar BMEP, lean ave. T_{IN}=494 °C, rich ave. T_{IN}=510 °C

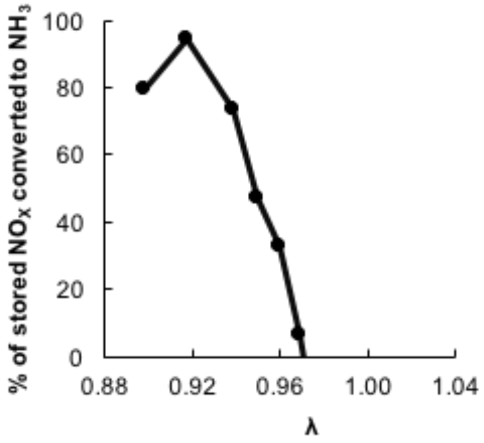

Figure 8. Stored NO_X to NH_3 conversion during rich phase of fixed load lean/rich cycling experiments at 2000 rpm 3 bar BMEP, lean ave. T_{IN}=393 °C, rich ave. T_{IN}=412 °C

For an estimation of the fuel consumption impacts of lean operation enabled by a passive SCR emissions control system, fuel consumption during lean/rich cycling is measured and compared to fuel consumption under conventional stoichiometric operation. Fuel consumption improvements for the fixed load and load step cycling experiments are shown in Figure 9. The maximum fuel consumption improvement was 5.1 % at rich λ = 0.98 and 7.9 % at rich λ = 0.97 for fixed load and load step, respectively. The maximum fuel benefit from running lean under these conditions is 11.3 %, which translates to 6.2 % and 3.4 % fuel consumption penalty for fixed load and load step, respectively. The lower fuel penalty in the load step cycling experiments is due to much higher engine out NO_X emissions during rich phase resulting in much shorter rich time and better fuel consumption. This underlines the importance of acceleration events during transient drive cycle operation, which create an opportunity for higher engine out NO_X emissions and, thereby, higher TWC NH_3 production, which reduces fuel consumption for a passive SCR system.

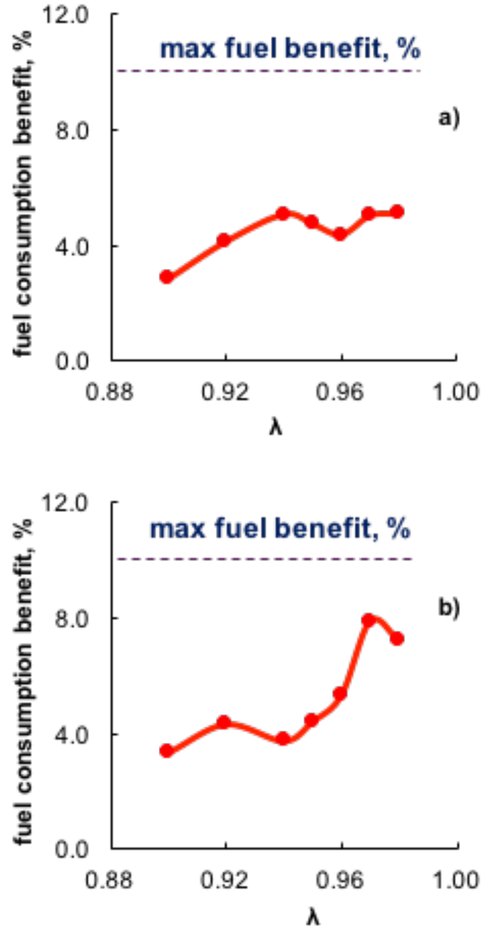

Figure 9. Fuel consumption benefits for a) fixed load (3 bar lean and 3 bar rich) and b) load step (3 bar lean and 8 bar rich) cycling experiments relative to stoichiometric engine operation as a function of rich λ.

Summary/Conclusions

In this work, the performance of the TWC with NO_X storage component was evaluated as a component in a passive SCR system. The key findings are as follows:

1. Passive SCR system fuel consumption is controlled by NH_3 produced while rich and NO_X concentration when lean
2. Passive SCR approach benefits from high engine out NO_X during rich operation and low engine out NO_X during lean operation
3. Rich phase λ controls engine out NO_X and NH_3 selectivity, which controls rich duration and fuel penalty
4. NO_X storage lengthens lean times by reducing NO_X slip and shortens rich times by increasing NH_3 production
5. Rich λ tip-in is a necessary step in driving the selectivity of the stored NO_X to NH_3
6. NO_X storage benefits are only realized at lower temperatures when NO_X is stored (<500 °C)
7. Higher engine loads associated with acceleration events create an opportunity for higher engine out rich NO_X, and high TWC out NH_3 and additional fuel efficiency gains

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Contact Information

Vitaly Y. Prikhodko, prikhodkovy@ornl.gov

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